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(54) Title: METHOD FOR PRODUCING A NANOTUBULAR CARBON MATERIAL, AND THE MATERIAL PRODUCED THEREBY



(57) Abstract: Nanoporous nanotube-like carbon can be produced in large quantities, with excellent yield and purity and at a low cost by a novel method involving the halogenation of aluminium carbide at a temperature above 450 °C, preferably about 500° to 800 °C, and most preferably at 550° to 750 °C. The nanotubular material exhibits nanotubes with the following approximate dimensions: length between about 6 and 50 nm, typically 14 to 22 nm; inner diameter between 5.5 and 27 nm, typically 10 to 14 nm; outer diameter about 6 to 30 nm; and total wall thickness of about 0.7 to 5 nm, typically 1.6 to 3.4 nm.



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METHOD FOR PRODUCING A NANOTUBULAR CARBON MATERIAL, AND THE MATERIAL PRODUCED THEREBY

TECHNICAL FIELD

5 The present invention relates to a method for producing nanoporous carbon materials with nanotube-like structures - here called nanotubes - in large quantities. The invention also relates to the nanotubular carbon material produced by said method.

BACKGROUND OF THE INVENTION

10 Explanations of frequently used terms in the area of fullerene materials

Fullerenes belong to a new type of carbon materials having new properties compared to crystalline carbon diamond, diamond like carbon, and graphite. The fullerenes are closed-cage carbon molecules with each carbon being bonded to three other carbon atoms tiling spherical or nearly spherical surfaces. The carbon atoms are usually arranged in hexagons or pentagons. 15 The most familiar and the smallest of these molecules is the Buckminster fullerene, C₆₀, having 60 carbon atoms of a structure resembling a soccer ball with equivalent covalent bonds. There are also higher fullerenes like C₇₀, C₇₆, C₈₂ and C₈₄ etc.

Carbon nanotubes are extended fullerene structures and are often referred to as buckytubes. They consist of concentric graphitic cylinders. The carbon nanotube takes almost 20 an infinite number of structures, being characterised e. g. by the diameter and the degree of helicity. The nanotubes can be either single- or multi-walled. The inner tube diameters are typically in the order of some nanometers, and the diameter of the outermost wall could be up to 20-30 nm. Typical aspect ratios (length to diameter) are about 50-100. The separation between the concentric walls are typically about 3.5 Å.

25

The nanotubular, nanotube-like material, according to the present invention and referred to hereinafter, is a porous carbon material consisting of nanotubes having multiple wall aggregates of short tubes that are intergrown with each other. See fig. 1 for the nanotube structure being built up by intergrown short and thick tube-like structures as shown in 30 transmission electron microscopy (TEM).

There also exists a nanoporous amorphous carbon material and a lamellar carbon material, described here for the purpose of comparison. The nanoporous amorphous carbon has a structure of interconnected hyperbolic carbon networks building up three-dimensional channel networks with narrow pore size distribution, and the nanoporous lamellar carbon has nanographitic lamellae with around 3-15 graphitic layers in each lamella, where the lamellae may be curved or not, and are interconnected by regions of amorphous carbon to form larger particles. These materials are not nanotube-like and do not belong to the fullerene family.

The thermochemical treatment according to the present invention and referred to hereinafter, is a treatment of a certain carbide or mixture of carbides in gaseous halogen or halogens at elevated temperatures to remove the carbide forming element and to produce a porous carbon material.

PRIOR ART

1. Prior art describing methods producing fullerenes, carbon nanotubes, hollow carbon fibres and similar carbon materials having nanoporous structures

Valuable summaries of the most usual prior art methods for fullerene production, separation and purification of carbon nanotubes and related materials has been presented by L.D. Lamb in "Fullerene Production", pages 20-34, "The chemistry of fullerenes", edited by R. Taylor, Advanced Series in Fullerenes Vol. 4, World Scientific, 1995 and by Harris in "Carbon Nanotubes and Related Structures ", Cambridge University Press, 1999. Basically, the standard method of fullerene production can be described as follows: an electric current is passed through electrode rods of amorphous carbon or graphite, striking a high current electrical arc between them, in an atmosphere of inert gas such as helium, nitrogen, argon or hydrogen. The rods are evaporated to a light fluffy condensate called fullerene soot. Under suitable conditions substantial fractions of the soot is comprised of fullerenes. The soot also comprises large quantities of carbon impurities such as graphite, amorphous carbon, carbon nanoparticles etc. Thus further extraction and separation of the fullerenes is necessary. This process pioneered the electric arc method for the production of fullerenes and it has since become a standard technique with a large amount of different variants, some of which will be described below.

The typical fullerene-soot generators of the above described methods can be divided into small bench-top chambers producing about a few tens of grams per day, and large high-

output chambers producing about hundreds of grams of soot per day. The small chambers are usually simple and of low cost. Larger chambers have several disadvantages, such as requiring more complicated equipment and several parameters being more complicated to control, e.g. the installation of rods, pump systems, generation of large amount of heat etc.

5 The prior art arcing methods are not easily scaled up to commercially practical systems.

Carbon nanotubes, also called buckytubes, are needle-like tubes produced by a similar arc-discharge evaporation method as described above. The needles grow on the cathode, and are comprised of multilayer coaxial tubes of graphitic sheets, with outer diameters up to 30 nm, and lengths up to a few micrometers.

10 Recently the method was further developed to produce a carbon plasma using a typical fullerene production apparatus resulting in carbon nanotubes mixed with nanoparticles. An arc discharge is accomplished by applying a suitable AC or DC potential between graphite rods and having a higher pressure of about 500 Torr¹ (200-2500 Torr) instead of the usual 100-200 Torr. The nanotubes are typically comprised of two or more concentric shells, with
15 diameters ranging from 2-20 nm, and lengths up to several micrometers, and the nanoparticles are typically tens of nanometers in diameter.

By that method the nanotubes and nanoparticles are formed under a broader range of conditions than do other fullerenes. There are however no ideal methods for separating these nanotubes from the nanoparticles (graphite and amorphous carbon). One carbon nanotube
20 separation method is to heat a carbon mixture at a temperature of about 750°C (600 - 1000°C) in an oxidising atmosphere to burn away the nanoparticles. The method leaves pure nanotubes but the starting material is consumed to a very large extent. The method has a low yield of carbon nanotubes, since the amount of graphite is so large and the difference in oxidising temperatures between them is not large.

25 An improvement of the production method has been made in order to get longer fullerenes. Fullerene fibres of 0.5 cm or longer can be produced by focusing a laser beam between the growing needle tip and the opposing electrode. A carbon feedstock is placed in the space around the electric field to provide the vaporised carbon. The needle electrode may be moved to lengthen the fullerene network to a fullerene fibre.

30 Other related techniques involve laser ablation of graphite, sputtering or electron beam evaporating of graphite, inductive heating of graphite, vaporisation of graphite powder in an Ar plasma jet and the use of concentrated solar radiation to vaporise graphite etc. The

common features are that pure graphite is vaporised in the presence of an inert quenching atmosphere, and that the product is a condensated fullerene bearing soot.

It has been reported that the production of single walled, small buckytubes has been performed in gram quantities. The presence of a transition metal Fe, Co, Ni as a catalyst is an important requirement. However, some of this catalyst metal will remain as an impurity in the final product. This is difficult to remove.

The products obtained by the known methods described above and the other variants of it, have a low content of fullerenes and a large amount of graphitic particles, carbon nanoparticles and amorphous carbon. Thus efficient methods for the extraction and separation of fullerenes are needed.

Another type of method is the forming of carbon nanotubes on a carbonaceous body (comprising fullerenes, graphite or amorphous carbon) by irradiating a surface of the shaped body with an ion beam to form a layer of carbon nanotubes on the surface by sputtering, resulting in a composite material.

Usually during the arc forming processes the anode is consumed, and it is necessary to move the electrodes to keep the gap width between them constant. An improved method of producing carbon nanotubes, is to submerge carbonaceous electrodes in liquid nitrogen or other suitable liquefied materials such as helium or hydrogen. A direct current is passed between the electrodes to strike a plasma arc between the anode and cathode that erodes carbon from the anode and deposits carbon nanotubes on the surface of the cathode. A mechanism for controlling the position of the electrodes that is situated in air above the liquid is used.

Although it is possible to use known techniques such as extraction with suitable solvents such as toluene, filtering, and chromatography techniques to separate the fullerenes and nanotubes from the fullerene soot, none of these methods are effective enough for large-scale separation. Solvent based extraction leaves residual amounts of solvents trapped in the interstices of the fullerenes that have been grown out of solution. Repeated sublimation in vacuum must be carried out. Chromatographic techniques are time consuming and not very effective. Significant amounts of the starting materials are lost, and the final product contains trace amounts of solvent trapped in the solid.

Another solution to the separation problem is to pulverise a mixture of nanotubes and graphite particles, to disperse them in a liquid and to centrifuge the liquid solution to obtain a

precipitate graphite phase and supernatant carbon nanotube and fine graphite phase. The supernatant is then divided into a solid and liquid phase. The solid phase is then heated in oxygen atmosphere to selectively burn away the graphite particles. The purity is improved but the method is complicated.

5 Yet another purification method includes reacting the mixture of nanotubes and graphite with a metal compound to intercalate the metal into the graphite; reducing the reaction mixture and converting the intercalated metal compound to elemental metal, and heating the reduction mixture at 450 - 600°C in an oxygen containing atmosphere to selectively oxidise the graphite and the elemental metal.

10 A process for purifying carbon nanotubes has been reported that avoids the disadvantages of conventional purification of nanotubes by oxidising under high temperatures (about 600-1000°C) that might be difficult to control. The purifying is carried out by reacting a mixture of nanotubes and carbon impurities with liquid phase oxidation, nitration or sulfonation agents at temperatures of about 120-180°C. The impurities are dissolved and the
15 nanotubes may then be separated, washed and dried. Further the nanotubes are reacted once again thereby dissolving carbon fragments (being carbon pentagon rings or carbon impurities) from the tips of the tubes.

In summary, the yield of nanotubes (mass of nanotubes relative to mass of precursor material), produced according to prior art methods, is rather low. Further, the purity (of
20 nanotube content) is not very high. Typical previously known production methods require elaborate refining methods that are costly, and often also reduce the yield. In view of the above, there remains a need of a method of producing nanoporous carbon materials consisting of nanotube-like carbon, or simply nanotubes, at a low cost, and in large quantities.

25 2. Prior art describing methods and processes where carbide precursor materials have been treated with gaseous halogens in order to produce porous articles

WO 98/54111 describes a production method for a porous carbon article, said method comprising the steps of first forming a work piece with microporosity, and then forming nanopores in the work piece by a thermochemical process at 350 - 1200°C. Materials having
30 controlled and predetermined nanopores, high mechanical strength, and complicated shapes may be produced. The nanopores generated during the thermochemical treatment process are

considered to be formed by ordered or disordered graphite planes of carbon, and to be shaped as slots.

WO 97/20333 describes a capacitor with a double electric layer with nanoporous carbon electrodes. The skeleton nanoporous electrodes are made by forming a silicon carbide body, with resin or pyrocarbon binders, saturating the body with liquid silicon at 1450 -1700°C, and treating the body in a gaseous halogen atmosphere at 900 - 1100°C. The possibility to use using Al or elements from the groups IV, V, VI of the periodic system of the elements is also mentioned in this document.

A similar method can be found in U.S. Patent 5,876,787 and U.S. Appl. No. 09/193,192 (being a divisional application of the U.S. patent), which describe a process of manufacturing a porous carbon material and a double layer capacitor using the same. The U.S. patent 5,876,787 discloses the method of producing the electrodes. The U.S. application 09/193,192 discloses the electrodes and the capacitor using the electrodes. The process involves forming a blank having a porosity of 30-50 % made of a carbide material of Si or metals from the groups IV, V, and VI of the periodic system of the elements. The blank is then deposited with pyrolytic carbon until the mass has increased about 10-25 %. The blank may optionally be saturated with liquid metal, e.g. Si at 1500 - 1700°C, before it is exposed to gaseous chlorine at 900 - 1100°C (for SiC), about 600°C (for TiC). During this step the carbide forming element and eventual metal from the saturation step is removed and pores are formed.

None of these documents disclose nanotubular carbon materials and neither mention or hint that such materials can be produced by heat treatment of carbides with gaseous halogens.

DEFINITIONS

For the claimed process and materials, the following definitions will be used:

Mass yield = The mass of the resulting material produced after thermochemical treatment of aluminium carbide related to the theoretical maximum mass of carbon. This mass may comprise nanotube-like material and other type(s) of carbon(s), residual carbide and possible impurities like aluminium oxide.

Theoretically, each kg of Al_4C_3 would result in, at the most, 250 g carbon.

Purity = By TEM estimated fraction of carbon nanotubes of the resulting material after thermochemical treatment, in percent of the resulting material.

SUMMARY OF THE INVENTION

The problems and shortcomings of the prior art are set aside by the inventive method and novel material according to the attached claims, which are hereby incorporated by
5 reference.

An object of the present invention is to provide a rapid, simple method for the production of nanotube-like carbon materials, which makes it possible to produce the material in large scale. The amount of produced nanotubes by the process depends on the capacity of the equipment (the size of the reaction sites of the furnaces), the heating and cooling of the
10 furnace, and also the diffusion of gaseous halogens and halogenides into and from the structure, all of which are controllable parameters in an industrial process by optimising the equipment and the processing parameters, for instance using equipment of a large capacity and of a "continuous" type (avoiding the interruptions by heating and cooling of the equipment). Thus the process gives large amounts of the produced nanotube-like carbon
15 material, with a high purity of nanotubes. The mass yield of the process is high, i.e. the losses of carbon material in the process are low. Further, the amount of unwanted by-products, produced in the process is also low. It is possible to increase the purity of the nanotubular material, i.e. the amount of the produced nanotubes even more by tuning the process parameters. Thus the process has the advantages of not being dependent of time consuming
20 extraction and purification methods.

A further object of the invention is to enable control of mass yield and purity of the nanotubular material produced. The mass yield and the desired purity of the material are to some extent interrelated. The process may be adjusted to give a material of very high purity of nanotubes, which may affect the mass yield, e.g. some carbon or nanotubes may be consumed
25 during a prolonged processing time. Vice versa, an extremely high mass yield may be achieved at some expense of purity.

Thus the process is suited for high mass yield and high purity because no need for special refining or purifying steps are required causing additional losses.

Also, the process is well adapted to production of nanotubular material in both particle
30 form (powder) and in the form of shaped bodies.

BRIEF DESCRIPTION OF THE ILLUSTRATIONS

The present invention will now be described with reference to the attached drawings, in which;

Fig.1 shows a TEM image of the nanotubular carbon structure synthesised from aluminium carbide (Al_4C_3) at 700°C ;

Fig. 2 shows schematically the crystal structure of Al_4C_3 ;

Fig. 3a shows a TEM image of nanotubular carbon synthesised from Al_4C_3 at 700°C ;

Fig. 3b shows a TEM image at low magnification of the nanotubular structure synthesised from Al_4C_3 at 700°C ;

Fig. 3c shows a TEM image of the nanotubular structure at higher magnification; and

Fig. 4 shows a TEM image of a carbon particle with amorphous structure chlorinated from Al_4C_3 at 300°C .

Fig. 5 shows a TEM image of a carbon particle with nanotubular structure chlorinated from Al_4C_3 at 600°C .

Fig. 6 shows an TEM image of a carbon particle of graphitic-like structure chlorinated from Al_4C_3 at 1100° .

DESCRIPTION OF THE INVENTION

The large scale synthesis of the nanotubular carbon material, according to the present invention is performed by halogenation of aluminium carbide at elevated temperature, causing the carbide forming element, aluminium, to leave the system as a halogenide, thus leaving a residue of porous carbon. The nanotubes may be synthesised from aluminium carbide of any form, like powders or formed articles (bodies).

In summary, the hitherto performed experiments have shown that:

- Nanotubes begin to form from aluminium carbide at furnace temperatures around and above 450°C and temperatures below 800°C are preferred.
- Thus, chlorinating aluminium carbide at furnace temperatures 500°C - 800°C , preferably at 550°C - 750°C , at the chosen process parameters produces a fundamentally

different structure than all other tested carbides. Instead of the nanoporous amorphous carbon, multiple wall nanotube-like structures, nanotubes in bulk are produced.

- The reaction between aluminium carbide and chlorine is exothermic, in order to avoid that the desired nanotubular structure transforms into the more graphitic lamellar type, the reaction must therefore be controlled. The synthesis of the nanotubes depend on the precursor particle size range, the batch size, the temperature, the time, the furnace type used etc.

- The purity of the produced nanotubular carbon is increased if the aluminium carbide is controlled for presence of oxide and is stored and handled in a way avoiding or minimising exposure to air, and especially humid air.

- Residual aluminium chloride can be removed from the nanotubular carbon by raising the temperature in Ar atmosphere and letting the chloride sublimate, and residual Cl_2 in the structure may be removed by treatment with H_2 , where Cl_2 is removed by forming HCl , which evaporates out of the structure. Other reagents are also possible.

- The purity of the process gases is important.

- Apart from the thermodynamic implication of the temperature, higher temperature gives faster reaction kinetics and quicker removal of the formed metal chloride from inside the structure through diffusion.

- Unsuitably long chlorination time at high temperature might oxidise the produced carbon to carbon tetrachloride.

Experiments of the present inventors have shown that chlorination of pure low carbon density carbides such as Mo_2C , having the $\alpha\text{-PbO}_2$ type crystal structure, gives nanoporous amorphous carbon lacking observable nanotube-like regions in the TEM studies, whereas pure carbides with higher carbon densities such as SiC (Wurtzite type hexagonal crystal structure) and TiC (rock salt type cubic structure) result in nanoporous amorphous carbon that may occasionally contain only trace amounts of nanotube-like structures in the surface areas and of onion-like carbon structure.

The porous carbon structures synthesised from SiC , TiC and Mo_2C (herein referred to as nanoporous amorphous carbon material) consist of interconnected hyperbolic carbon networks building up porous 3-dimensional channel networks with a narrow channel size

distribution. The pore sizes are a result of the carbon sub-structure of the precursor carbide, which results in smaller nanopores for SiC and TiC, whereas Mo₂C has larger pores.

In the nanoporous amorphous carbon synthesised from pure SiC, and group IV, V or VI elemental carbides like VC and TiC etc. (chosen e.g. for their ability to form halogenides being non-harmful to the produced carbon) none or only trace amounts of nanotube-like material were found when observed in TEM. A large number of experiments were made trying to increase the fraction of nanotube-like material. Experimental conditions such as temperature, gas flow and time were varied but none of these exhibited the desired nanotubular structure.

Thus, our experiments indicate that aluminium carbide is the only carbide suitable for the forming of nanotubes in a large scale by halogenation.

A possible explanation for this is that the distribution of carbons in aluminium carbide is optimal for forming local graphitic layers, and the alternation between aluminium in the mixed hexagonal and cubic packing opens the possibility for slabs of graphitic layers to roll up and connect in nanotube-like structures. Since carbon formed through a chlorination reaction of carbide is strongly dependent on the distribution of carbon in the carbide, and since nanotube-like structures consist of curved graphitic planes it is assumed that a carbide with the possibility of forming graphitic planes, and with a non-uniform layer structure, opening the possibility for slabs of graphitic planes to roll up to cylinders, is necessary.

Aluminium carbide, Al₄C₃, is the only carbide formed by aluminium, and it has a crystal structure consisting a mixture between hexagonal and cubic close packing of the carbons, with aluminium residing in layers of carbon tetrahedra. See figure 2 showing the crystal structure of Al₄C₃. The black spheres are the C atoms inside the tetrahedra and octahedra, with Al at the vertices.

The synthesis of the nanotubular carbon material from aluminium carbide precursor is performed with the following steps, some of them being only optional, i.e. not necessary for the formation of the nanotubular structures:

Thermochemical treatment

A thermochemical treatment is applied to either carbide powder in particle form or to a body produced according to any of the optional steps according to the embodiments described

above. The thermochemical treatment is carried out in a medium of gaseous halogen or halogens at elevated temperatures, preferably 450°-800°C, creating volatile halogenides of the carbide forming element (e.g. Aluminum chloride). The aluminium carbide is transformed to porous carbon, and the formed halogenides are removed from the material, e.g. by the halogen gas flow or by washing in Ar gas.

The nanotubes are formed by the halogenation of the aluminium from the aluminium carbide at certain synthesis conditions. When the halogenisation is performed at a most preferred limited temperature range around 550°-750°C, the resulting nanoporous bulk structure is comprised of short, thick, multi-layer nanotubes entangled and interconnected to each other. In the case when the precursor aluminium carbide has been deposited with pyrocarbon, the resulting material comprises nanotubular particles bonded by pyrocarbon, unless the optional step of purification above has been applied.

If the halogenisation is performed at lower temperatures, at temperature range of around 200°-450°C, the resulting structure is a nanoporous amorphous one, similar to the structures obtained from halogenisation of e.g. silicon carbide or titanium carbide.

If the halogenisation is performed at higher temperatures, at temperature range of around 800°C and higher, the resulting nanoporous structure is a mixture between amorphous and lamellae structure parts; the graphitic characteristics increasing with increasing temperature. These structures contain nanographitic lamellae with around 3-15 graphitic layers in each lamella, where the lamellae may be curved or not, and are interconnected to form larger particles.

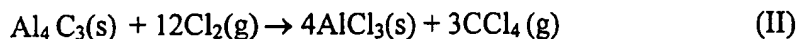
The halogenation is carried out similarly to other known methods. The halogens and halogenides do not normally react with the formed carbon under the given temperature conditions. The process time may be adjusted depending on the accentuation of a high yield or a high purity.

When gaseous chlorine is used the treatment is carried out at a furnace temperature, i.e. the set temperature for the furnace, of 200°-1200°C. The different nanoporous carbons are formed at the removal of volatile chlorides of the aluminium in accordance with the chlorinating redox reaction:



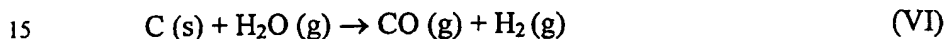
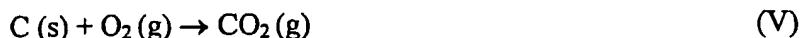
Basically the chlorination is performed by leading a Cl_2 (g) stream over the aluminium carbide at an appropriate temperature. It is essential that the carbide forming element, aluminium, forms a volatile chloride. The volatile chloride is lead away from the reaction site by the gas stream.

5 Possible unwanted side-reactions are



A reaction according to formula II occurs at quite high temperature, whereas reaction III can occur for the formed nanoporous carbon at temperatures around 800°C , and above.

10 Another undesirable reaction involving the formed nanoporous carbon is oxidation of carbon with H_2O or O_2 (which may occur as impurities in Ar and Cl_2 gases) to CO and CO_2 , according to formulas IV, V and VI:



The formed H_2 in the reaction according to formula VI can react with the carbon and give hydrocarbons and, because of the presence of chlorine, hydrochlorocarbons.

Studies by the present inventors have shown that one important aspect of the process parameters is controlling the purity of the inlet gases, i.e. to purify Ar from O_2 , and Cl_2 from
20 oxygen and water, e.g. with filters etc.

The halogenation reaction of the present invention is simple and proceeds rapidly, which make possible large scale production and the method is new for the production of nanotube-like carbon materials.

Theoretically, each kg of Al_4C_3 would result in, at the most, 250 g carbon. From the
25 presently available experimental mass yields and estimated levels of purity, this would give 200g nanotubes (80%) at a synthesis temperature of around 700°C . With optimisation of the process, it is possible to arrive at even higher mass yields at higher purity and to accentuate either very high purity or very high yield, or even both at the same time.

The mass yield is dependent of the quality of the reactants and can be increased with higher purity of the inlet gas, and by optimising the reaction time and the flow of the inlet gases. The purity also by not exposing the Al_4C_3 to air, and by evaporating residual AlCl_3 out of the carbon by increasing the temperature.

- 5 The mass yield may be controlled but to some extent at the expense of purity; not sacrificing any initial carbon material may result in not quite perfect purity because of difficulties in absolute fine tuning of time and temperature.

If desired, the process may give a nanotubular material of lower purity by changing the process parameters.

10 Forming of a body (optional step)

- According to one embodiment, the aluminium carbide can be formed to a work piece before further treatment. The forming step of the aluminium carbide particles to a work-piece is achieved by any known method, e.g. by pressing with or without a temporary binder or an organic binder that leaves a carbon residue, by using slip, tape or slurry casting, by using
15 injection moulding, or partly sintered by known high pressure, high temperature techniques or using pulsed high currents. The binder is then evaporated or hardened after the forming step.

- The size and shape of the initially formed work piece is retained during all the different steps to the final body. The work piece porosity and the pore size range are chosen to obtain executability of the following process step(s) and are dependent upon the chosen method of
20 forming the work piece and on particle size(s).

Deposition of pyrocarbon (optional step)

- According to another embodiment, the powder or work piece of the aluminium carbide material is further subjected to a treatment in a medium of gaseous hydrocarbon or
25 hydrocarbon mixtures at a temperature exceeding the decomposition temperature of the hydrocarbon(s). During the decomposition of hydrocarbon(s), pyrolytic carbon, also known as pyrocarbon is deposited on the particles or on the surface and in the pores of the work piece thereby forming an intermediate body.

- This step is performed to achieve an additional bonding of the carbide particles into a
30 continuous, rigid, porous skeleton structure. The duration of the treatment in the said medium

is decided by the mass increase and controlled by measuring the mass of the powder or work piece, and the intermediate body.

The process is completed when the strength of the body has increased to the desired level, which usually occurs after the mass has been increased by a few percent.

5 The hydrocarbons used during the treatment in hydrocarbons medium may be selected from the group of acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives. The temperature range is about 550-1200°C, the optimal decomposition temperatures for each of these hydrocarbons falling within this range. Alternatively natural gas may be used as a mixture of hydrocarbons and the temperature range used is 750-950°C.

10 The formed intermediate body or intermediate powder is a rigid carbonaceous skeleton comprising aluminium carbide particles bonded by the deposited pyrocarbon. The skeleton structure is kept throughout the following process steps, to the final material.

Purification (optional step)

15 According to a further embodiment of the invention, a purification step may be included. If the shaped body according to anyone or both of the above embodiments contains carbon bonding the carbide particles (which is the case when pyrocarbon has been applied and when an alternative binder is decomposed to carbon) a pre-treatment purification step is used.

20 The porous work piece, or intermediate body or intermediate powder is infiltrated by liquid or gaseous aluminium in vacuum or argon. The carbon in the work piece, or intermediate body or intermediate powder will then react with the aluminium to form aluminium carbide (secondary), thus creating a composition of primary and secondary aluminium carbide with some excess free aluminium.

25 To achieve a good quality, desired size and shape of the work piece, the intermediate body and the final body, consideration must be paid to the following:

- (a) the particle size(s) of the initial aluminium carbide,
- (b) the amount of binder material incl. pyrocarbon, and
- (c) the method of forming the work piece.

30 Such a combination of these factors is chosen that will allow infiltration of liquid or gaseous aluminium; the work piece porosity and pore size range is thus controlled.

2. Description of the nanoporous carbon material according to the invention

The nanotubes according to the present invention are shorter than many reported
5 nanotubes, and rather barrel-like. The nanotubes are thick with multiple walls, varying
between 2 and about 15 layers.

The structure of the novel nanotubular carbon consists of intergrown nanotubes, i.e.
each nanotube is connected to at least another nanotube. The nanotubes are short and thick
tube-like structures, rarely perfectly cylindrical. In other words, there can be some angle
10 between the nanotubes indicating a somewhat polyhedral shape.

Typical ranges and sizes in the nanotube structure are inner diameters in the orders of
5.5-27 nm, typically 10-14 nm, outer diameters of about 6-30 nm, typically 14-19 nm,
distance between inner and outer diameter 0.7-5 nm, and length of the nanotubes 6-50 nm,
typically 14-22 nm. The number of walls is 2-15, typically 5-10. The distance between the
15 walls is about 0.335 nm, which results in the stated total wall thickness of about 0.7-5 nm, and
typically of about 1.6-3.4 nm.

If desired, the inventive method includes possibilities to adapt the shape of the final
product by the forming the work pieces and intermediate bodies and machining of those. The
final body produced by the described method thus has a predetermined shape and size.

20 The different synthesised carbons have been examined in high resolution transmission
electron microscopes (TEM). A large number of nanotubular samples have been studied with
TEM, and it is clear that the bulk of the nanotubular material consists of the structure of
intergrown nanotubes. In very rare cases onion structures was found, but the extent of these
are negligible. These observations are consistent in all examined samples processed using the
25 preferred processing parameters.

Figure 3a shows the edge of a particle of nanotubular carbon from Al_4C_3 synthesised at
700°C, where short and multiple wall nanotubes lie in different orientations.

Figures 3b and 3c show another particle synthesised at 700°C at different
magnifications, where the walls of the nanotubes are more clearly seen. The tubes are not
30 isolated from each other, but are normally intergrown, thus forming solid networks with
mechanical stability.

The exact size and number of walls differ from nanotube to nanotube, but optimising the experimental conditions may produce a more uniform material. It is, for instance, desirable to minimise the possible oxidation during prolonged processing times.

Hence, chlorination of aluminium carbide is a method for the bulk synthesis of amorphously ordered carbon nanotubes, being a completely unique method and material. Al_4C_3 has shown to be the only precursor carbide giving bulk amounts of nanotube-like structures, whereas all other tested carbides gave nanoporous amorphous networks of interconnected carbon channel structures with different bulk densities and pore sizes.

The claimed concept is further elucidated with the following examples.

EXAMPLES

In the following examples, mass yield was calculated according to the following formula:

$$\text{Mass yield} = m_{\text{product}} \times M_{\text{Al}_4\text{C}_3} / (3 \times m_{\text{Al}_4\text{C}_3} \times M_{\text{C}})$$

wherein m denotes the mass and M the molar weight;

Purity is estimated from the TEM investigations of a large number of fragments in each of the specimens.

According to one embodiment of the invention, the following typical steps are used in the production of nanotubes in particle form:

1. An appropriate amount of aluminium carbide is weighed (typically abt. 2 g for laboratory scale), the sample is inserted into a reactor in a furnace, e.g. a quartz-glass reactor tube,

2. the system is flushed with Ar gas to lead away the air,

3. the furnace is heated in a stream of Ar gas,

4. the gas flow is switched from Ar to Cl_2 process gas at a stable desired temperature, and the reaction is allowed to proceed during a chosen time (usually 30 - 60 min).

5. After full reaction time, the system is switched back to Ar gas and kept at the reaction temperature for typically one hour to allow the metal chloride to diffuse out of the nanoporous carbon, and a subsequent short thermal treatment at an increased temperature to diffuse all possible residual metal chloride and chloride gas.

6. the furnace temperature is decreased to room temperature, and

7. the resulting material is retrieved from the reactor and examined e.g. by weighing, SEM, XPD, TEM, gas porosimetry, and BET.

Naturally, the above steps can be supplemented with additional steps, such as pre-treatment, forming of a work piece, deposition of pyrocarbon, and purification, as described above as optional embodiments of the present invention.

Example 1.

Chlorination of Al_4C_3 (Lot. A18K02) from Johnson Matthey GmbH, Alfa Aesar, Germany, at temperatures from 200 to 1200°C was carried out. The purity (assay) of the carbide was 99+% and the average particle size (APS) was 4 micrometers. The chlorine gas with the purity up to 99.8%, argon with an assay 99.998% and carbon dioxide were provided from AGA corporation, Estonia.

A thin layer (~2mm) of carbide powder (~2.1g) on a quartz cuvette (area ~50cm²) was placed in quartz reactor (Ø 90mm) and kept in the argon flow for 1h at room temperature to remove O₂. The chlorine flow was started when the reactor chamber reached the desired temperature. The chlorination time was 1h in all experiments. Dechlorination was performed by argon flow at 1000°C for 1h. In all experiments reduced argon flow continued until the reactor cooled down to the room temperature.

The mass yield, as determined by weight, of the resulting material retrieved from the carbide was quite close to theoretically estimated maximum carbon values.

Table 1 summarizes some characteristics for different nanoporous carbon samples synthesised from Al_4C_3 .

TABLE 1

A summary of the analysis of carbon materials obtained by chlorination at different furnace temperatures. The measured specific surfaces, the relative yields and the α -angles by XRD (defined in text) are given.

5

Furnace temperature (°C)	Relative yield (%)	XRD α -angle (°)
400	97	16.7
450	97	16.5
500	97	10.0
600	97	8.0
700	90	6.5
800	71	5.0
900	91	4.5

15

Previously, it has been shown that the slope of the diffraction line at small angles of diffraction is proportional to the relative amount of the carbon mono-layers joined in graphite-like structure fragments in carbon [Kravchik et al. Zh.P.Ch. 1989, 2430-2435]. The XRD spectra of carbons investigated in this study showed also that the intensity of 002 peak was related to the angle between diffraction line and the base line of diffractogram – the smaller angle the higher intensity of 002 peak. In table 1 is shown the angle (α) of the carbon diffraction line vs. chlorination temperature for different nanoporous samples of Al_4C_3 .

25

The plot of the angle α vs. chlorination temperature reveals that the carbon made at below 500°C has a similar, almost amorphous structure. At about 500°C the α significantly drops and decreases with increasing temperature. Very small α value (4°) at 900°C corresponds to the structure where almost all carbon mono-layers have been reoriented to form the graphite-like multi-layers. Above 900°C the α reaches an almost constant value at 1100°C. Observations in TEM was the most important tool for observing the occurrence of nanotube structures and to establish purity.

30

Conclusions:

The 200–300°C samples are completely amorphous as evidenced by figure 4.

The 400°C samples are amorphous with high surface areas, whereas in 450°C samples some traces of nanotubular structures were observed.

5

In the 500°C sample the 002 peak is almost absent in XRD diffraction, however α decreases substantially as it also happens with BET surface area. α is the angle between base-line and the background at small angles of diffraction, and is shown to be proportional to the amount of amorphous carbon [Kravchik et al. Zh.P.Ch. 1989, 2430-2435]. This indicates that formation of nanotubes may have started.

10

In the 600°C sample, TEM studies confirm the presence of both amorphous and nanotubular structures. That nanotubular structure dominates as evidenced by Fig. 5.
The obtained material consists of practically pure carbon.

15

The 700 – 800°C samples show intensive 002 peak in XRD. The surface area ($\sim 600\text{m}^2/\text{g}$) by BET indicates that the carbon consists of a very high percentage of multi-walled nanotube-like structures, which is confirmed by TEM observations. Main difference between 700 and 800°C carbons is that majority of the barrels in first one seems to be closed whereas these are opened in the latter. Surprisingly low mass yield indicates that at 800°C the C+Cl₂ reaction activation energy is reached for the more active amorphous carbon and/or nanotube caps (five-ringed carbon structures).

20

For samples processed at 900°C and higher temperatures all studied characteristics stay constant at these temperatures. The high mass yields compared to the 800°C sample reveal that the carbon is not highly reactive.

25

Fig. 6 shows a TEM image of a carbon particle of graphitic-like structure elements chlorinated from Al₄C₃ at 1100°C.

In summary, the experiments show that the mass yield is above 70%, and that mass yields above 85% and even above 90% are reachable. Also, in the samples with nanotubes the purity is usually between 70 and 90 %, reaching a peak for Al₄C₃ processed at 700°C, as estimated from TEM observations. Lower purity is also achievable.

30

These examples are only illustrative and not limiting.

Characterisation methods

The following methods for characterisation and examination of the produced
5 nanotubular materials were used: X-ray Powder Diffraction (XPD), Scanning Electron
Microscopy (SEM) and Transmission Electron Microscopy (TEM).

XPD is an X-ray technique performed on powders, and reveals the content of different
crystalline phases due to diffraction of the X-rays in the crystals. Each single phase shows up
as a unique finger print of the structure, and XPD is therefore of big use in characterisation of
10 solids. Amorphous compounds do not produce sharp diffraction patterns, why the method is
used for the system here to make sure that the samples are devoid of crystalline phases, such
as the carbide starting material.

Electron microscopy is analogous to normal light microscopy, but can magnify much
higher since electrons are used instead of light, and magnetic lenses instead of glass lenses.
15 SEM is the technique used to study the morphology of particles. It is often combined with
energy dispersive X-ray analysis (EDX), a method to analyse the X-ray emitted from the
sample when it is irradiated with electrons, which gives the content of the different elements
present in the sample. The JEOL 880 instrument used in this study is particularly effective
since it has a technology which allows detection of very light elements, such as carbon. This
20 means that it is possible to distinguish between e.g. a particle of Si from one of SiC.

In TEM the electrons pass through a small fragment of the crushed sample, and an
image of the atomic structure can be recorded. With perfect conditions and a crystalline
sample, atomic resolution can be obtained, but this is not possible with amorphous samples
due to the low ordering. Also, being a very light element, carbon gives low contrast. Three
25 TEM instruments have been used; a JEOL 200 CX, a JEOL 3010 and a Philips 200 kV FEG.

SUMMARY

By the inventive method it is possible to easily produce nanotube like materials e.g.
nanotubes on a large batch scale. By this method, high purity and high yield can be reached. It
30 is also possible to control the levels of yield and purity.

Furthermore, the present method, besides the advantages presented above, also makes possible the production of bodies of complex shapes – when desired - with minimum machining required. Owing to their high mechanical strength, the bodies according to the invention can be used under conditions demanding retaining of their shape. Refining by
5 means of creating secondary aluminium carbide is possible.

The nanotubular carbon material according to the invention can find wide application e.g. for energy storage, for adsorption and microdosage of substances, for purification and separation of cryogenic liquids and gas mixtures, etc. because of their advantageous properties, and especially their specific nano-structure.

10 The foregoing description of the invention, with specific embodiments thereof, has been presented for the purpose of illustration and description. The description and examples are not intended to be exhaustive or to limit the invention to the precise forms disclosed, and obviously many modifications, embodiments, and variations are possible in light of the above teaching. It is intended that the scope of the invention be defined by the Claims appended
15 hereto and their equivalents.

CLAIMS

1. A method of producing nanoporous carbon materials with nanotubular structure, comprising the step of treating a carbonaceous precursor material of optional shape at elevated temperature in a gaseous halogen atmosphere in a reactor, said carbonaceous precursor material being aluminium carbide, Al_4C_3 .

2. The method according to claim 1, wherein the reactor and precursor material are flushed with an inert gas prior to halogenation.

3. The method according to claim 1, 2 or 3, wherein the halogen gas is chlorine gas.

4. The method according to claim 1, 2, 3 or 4, wherein the halogenation is performed with a mixture of halogen gas and inert gas, preferably a mixture of argon and chlorine.

5. The method according to any one of claims 4 - 5, wherein the chlorine gas is of a purity of or exceeding 99.8 %.

6. The method according to any one of claims 1 - 6, wherein the halogenation is performed at a furnace temperature of above 450°C , preferably at 500° to 800°C , more preferably at 550° to 750°C .

7. A method of producing nanoporous carbon materials with nanotubular structure, comprising the step of treating a carbonaceous precursor material of optional shape at elevated temperature in a gaseous halogen atmosphere in a reactor, wherein said carbonaceous precursor material is aluminium carbide, Al_4C_3 and said material is deposited with pyrocarbon and infiltrated with molten or gaseous aluminium prior to halogenation.

8. The method according to claim 8, wherein the halogenation is performed at a furnace temperature of above 450°C , preferably at 500° to 800°C , more preferably at 550° to 750°C .

9. The method according to claim 8, wherein the halogen gas is chlorine gas.

10. The method according to claim 8, wherein the halogenation is performed with a mixture of halogen gas and inert gas, preferably a mixture of argon and chlorine

11. The method according to any one of claims 1 - 11, wherein nanoporous carbon with nanotubular structure is produced in a mass yield exceeding 70 %, calculated according to the formula

$$\text{Mass Yield} = m_{\text{product}} \times M_{\text{Al}_4\text{C}_3} / (3 \times m_{\text{Al}_4\text{C}_3} \times M_{\text{C}})$$

wherein m denotes the mass, and M the molar weight.

12. The method according to any one of claims 1 - 12, wherein nanotubular carbon is produced in a purity exceeding 70 % .

13. A nanoporous carbon material comprising intergrown nanotubes to at least a purity of 50 %.

5 14. The nanoporous carbon material according to claim 14, wherein the purity is above 70 %.

15. The nanoporous carbon material according to claim 14, wherein said nanotubes have the following dimensions: length between about 6 and 50 nm; inner diameter between 5.5 and 27 nm; outer diameter about 6 to 30 nm; and total wall thickness of about 0.7 to 5 nm.

10 16. The nanoporous carbon material according to claim 14, wherein said nanotubes have the following dimensions: length between about 14 to 22 nm; inner diameter between about 10 to 14 nm; outer diameter about 14 to 19 nm; and total wall thickness of about 1.6 to 3.4 nm.

15 17. The nanoporous carbon material according to claim 14, wherein the purity is 90 % or more.

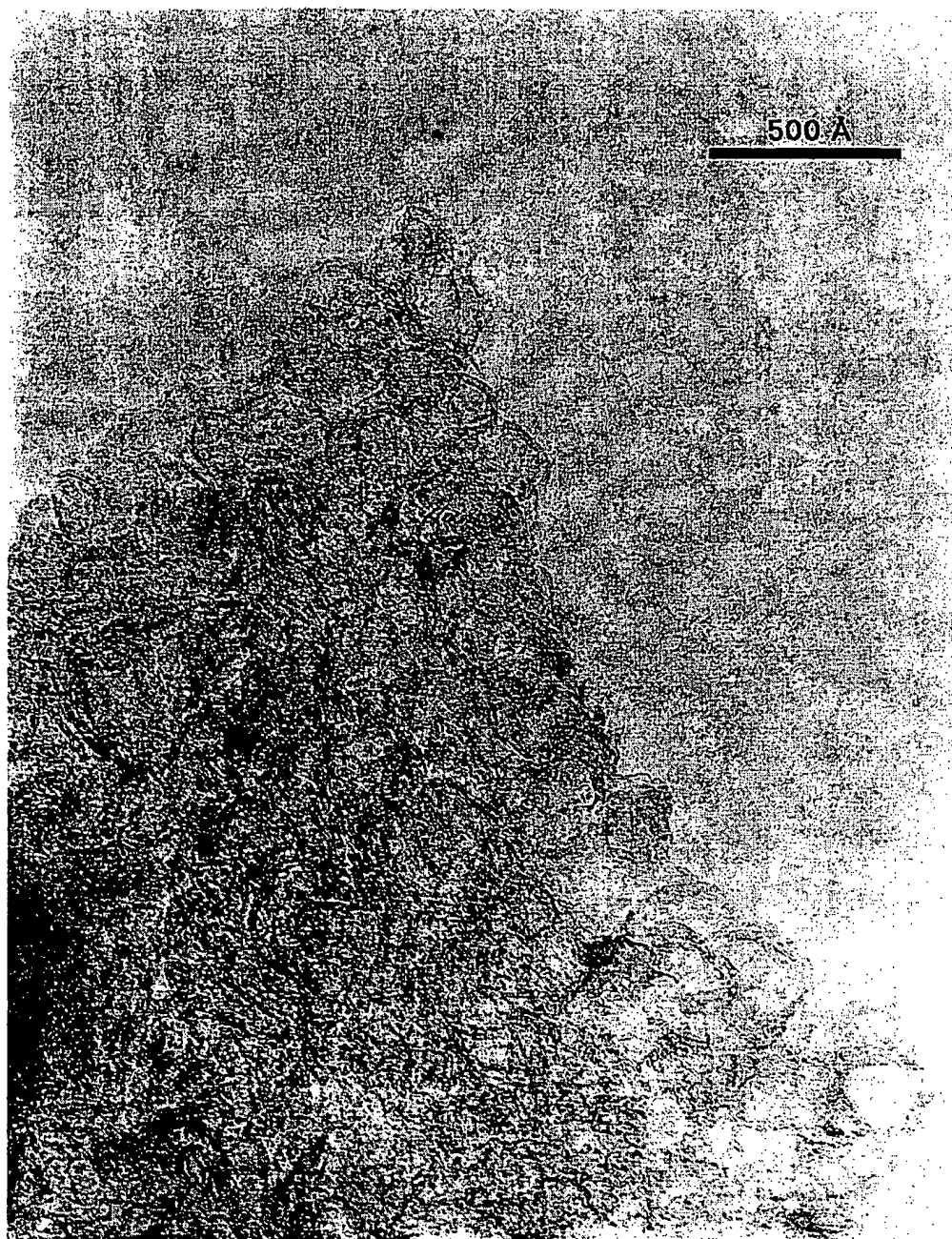


FIG. 1

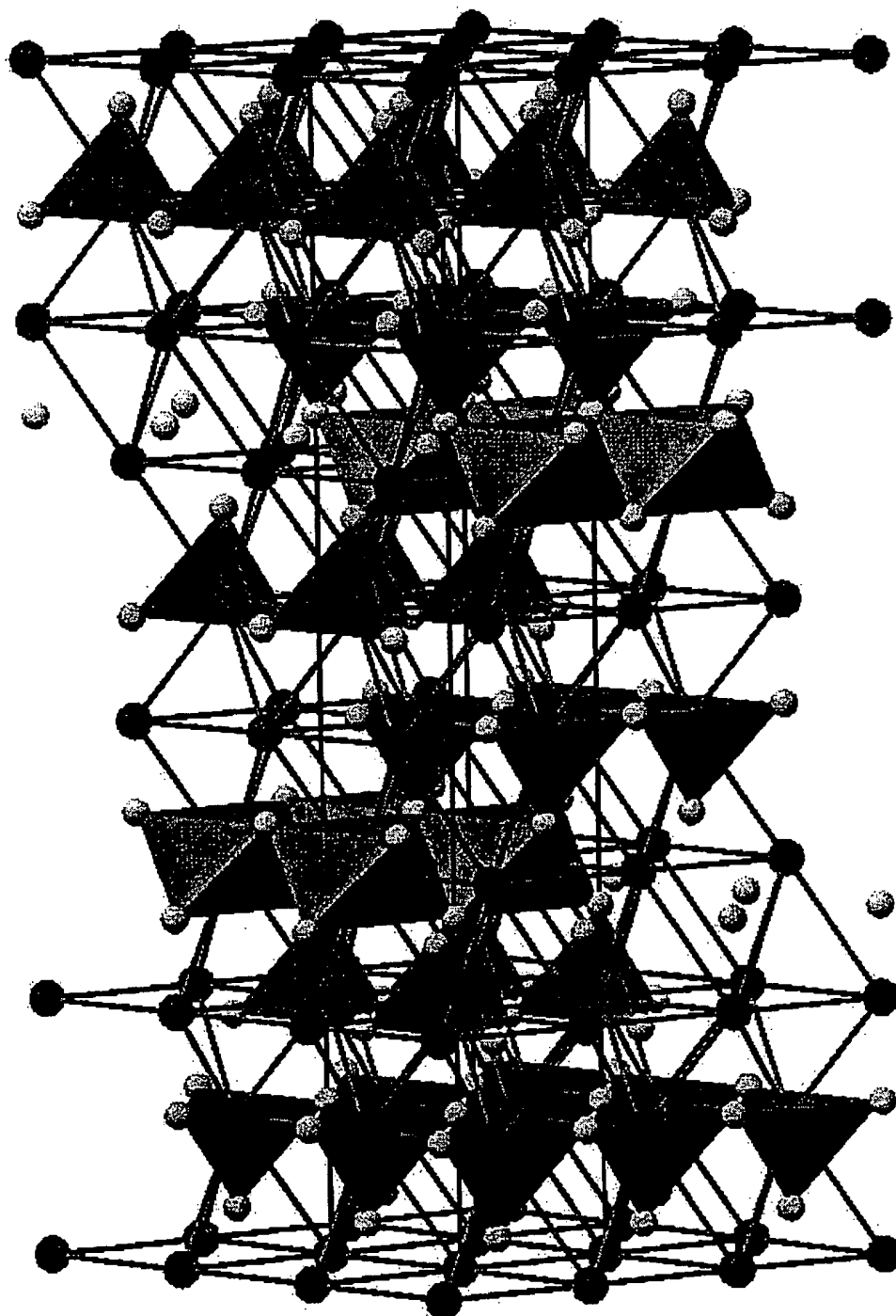


FIG.2

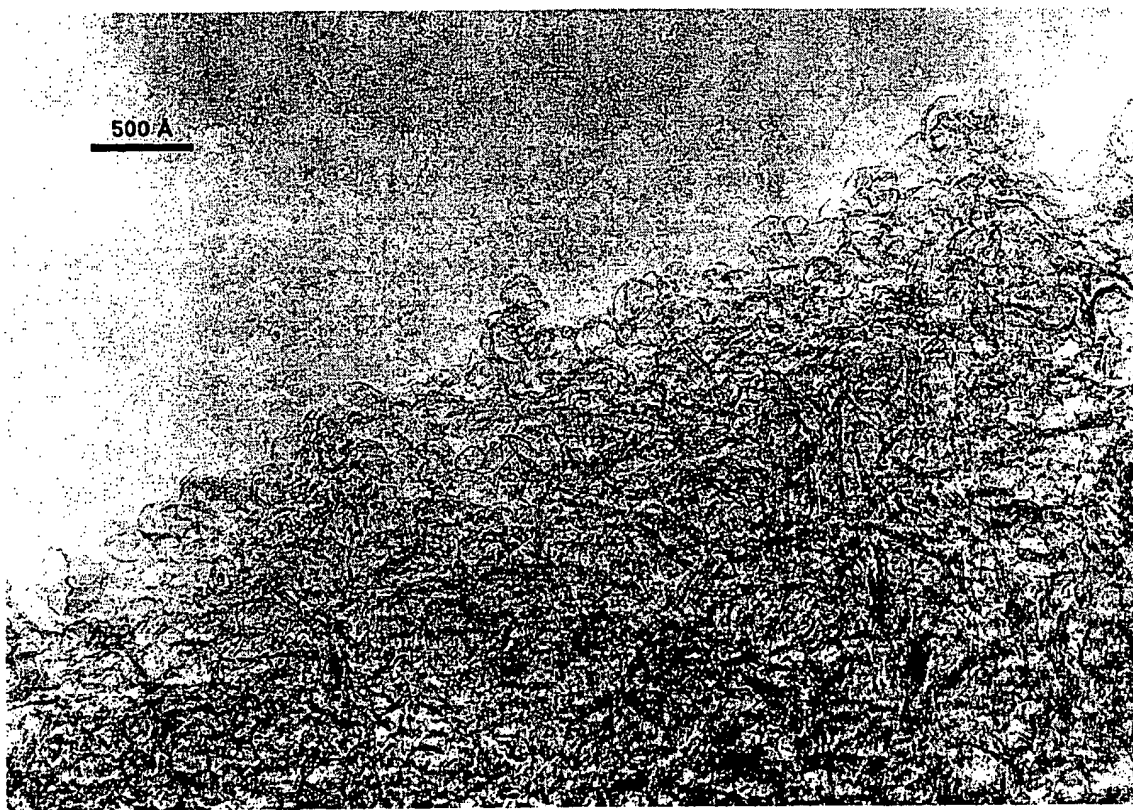


FIG. 3 a

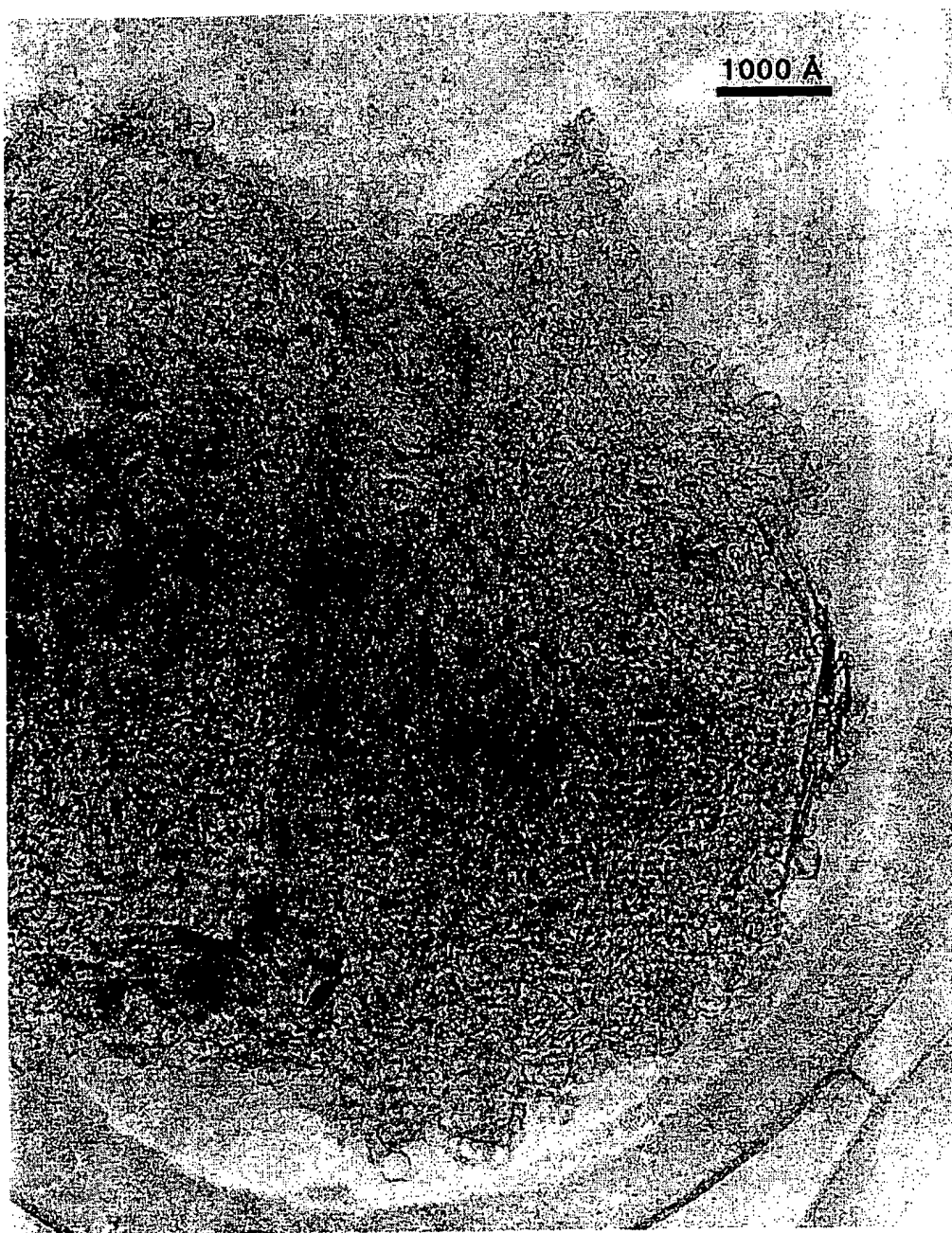


FIG. 3 b

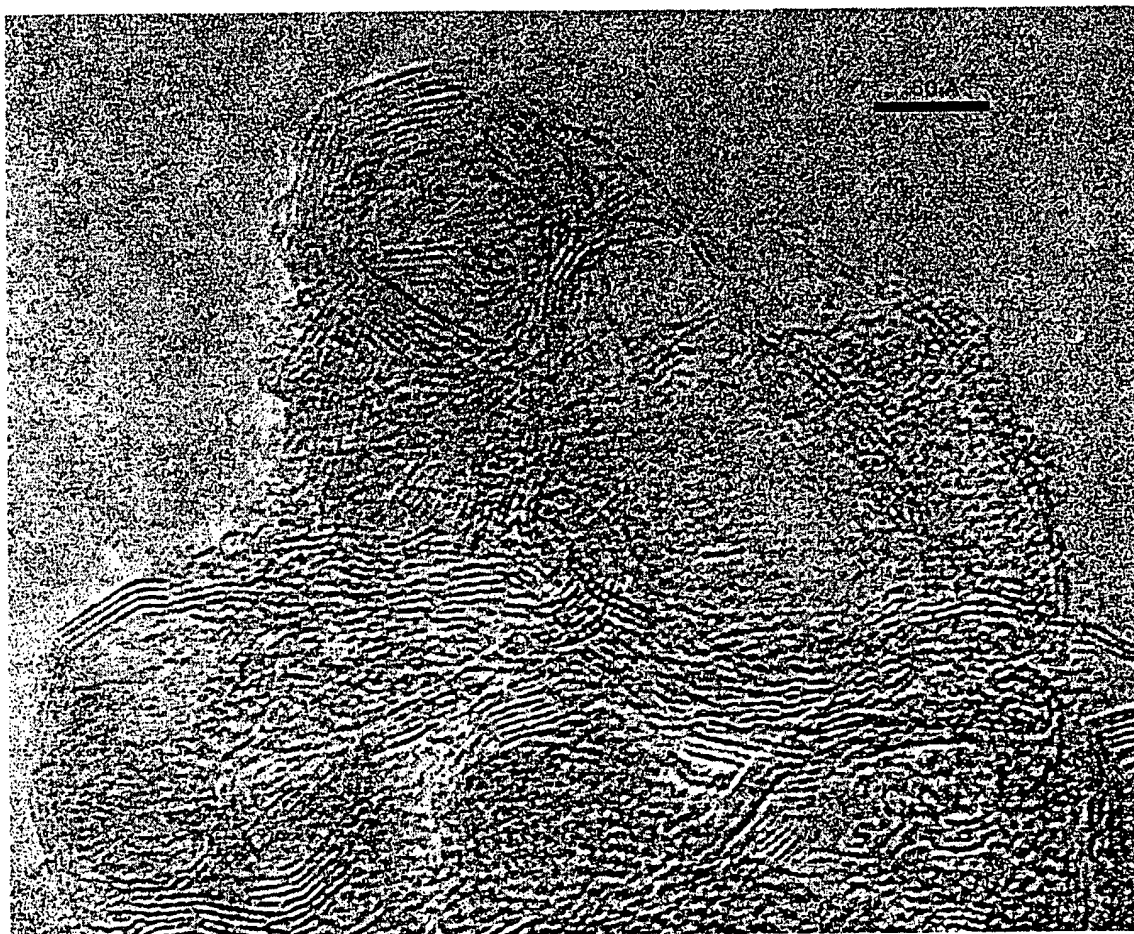


FIG. 3 c

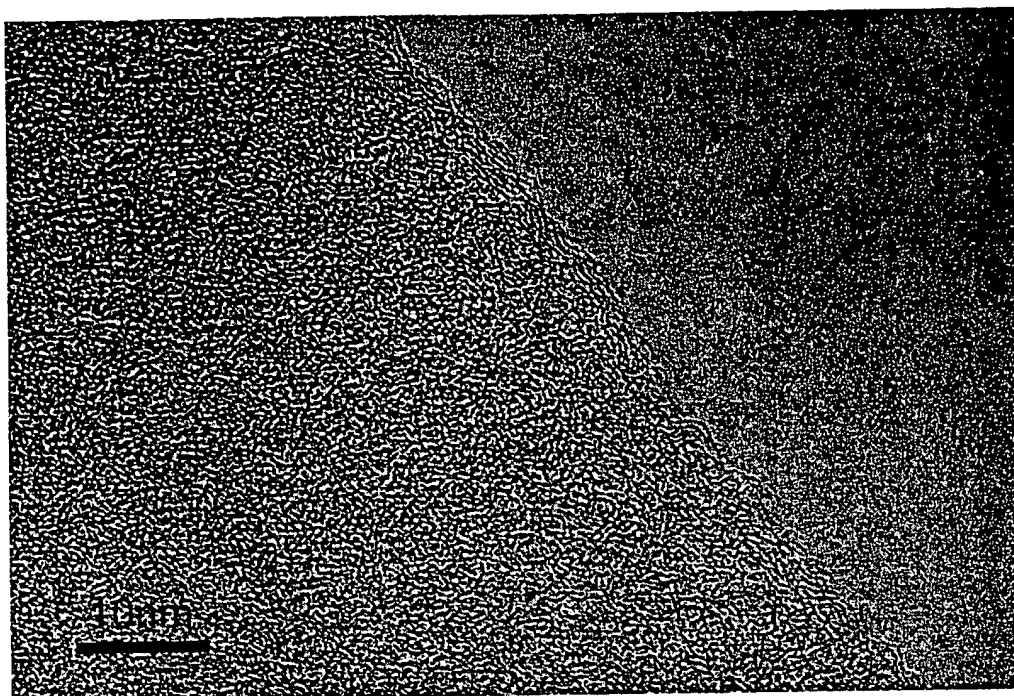


FIG. 4

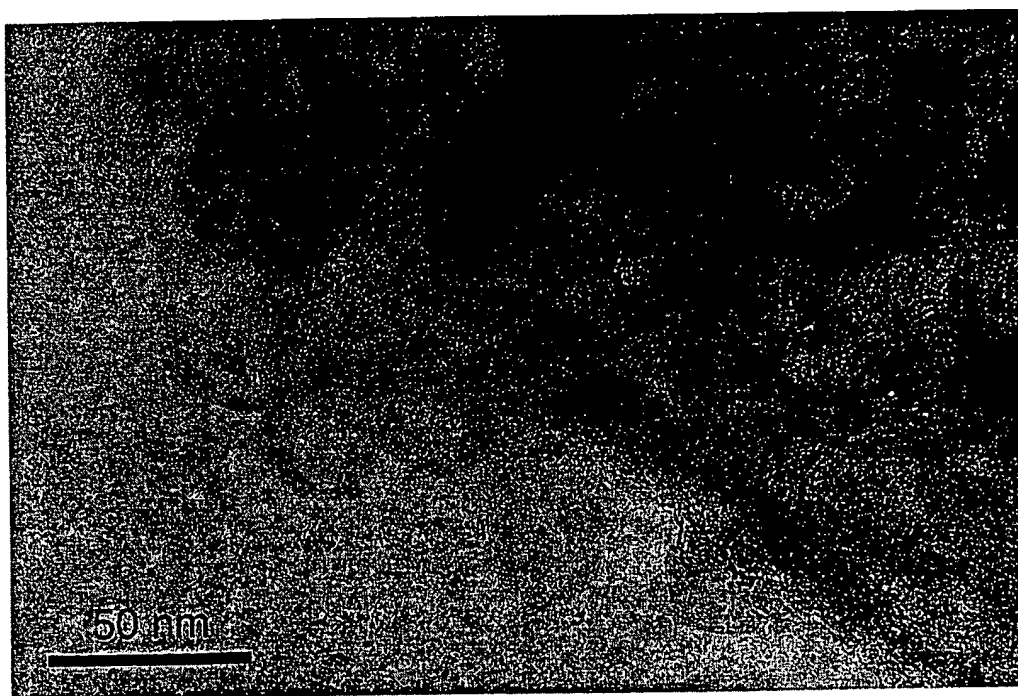


FIG. 5

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FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/08424

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B31/02 C04B38/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

2 February 2001

Date of mailing of the international search report

13/02/2001

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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